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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.

THE ELECTROCHEMICAL EQUIVALENTS OF  
COPPER AND SILVER.

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FOUR years ago we began an investigation which had as its object the careful study of the well known irregularities of the "copper voltameter" from the point of view of the modern theories of electrochemistry. One reason for this study was the fact that the atomic weight of copper computed from the relation of its electrochemical equivalent to that of silver was noticeably smaller than the atomic weight obtained in this Laboratory by purely chemical methods.\* Owing to circumstances beyond our control the completion of the work was postponed far beyond its proper time; but at last it is in a condition suitable for partial publication. The matter was complicated by the discovery of an error in the "silver voltameter," as well as in the "copper voltameter." In the mean time an extremely interesting paper by Foerster and Seidel, and several other valuable contributions by Kahle, Patterson and Guthe, and others, upon allied subjects, have appeared.† These cover a part of the ground occupied by our work, and thereby shorten the present account. The work naturally falls under two headings, because each metal needed its special investigation; and this natural division will be retained in the following description.

I. THE COPPER VOLTAMETER.

The work of Gore, Lord Rayleigh and Mrs. Sidgwick, Gray, Shaw, Vanni, and Gannon,‡ showed long ago that a side reaction, varying in

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\* T. W. Richards, *These Proceedings*, **26**, 240 (1891).

† Foerster and Seidel, *Zeitschr. anorg. Chem.*, **14**, 106-140; K. Kahle, *Wied. Ann.*, **67**, 1 (1899); Patterson and Guthe, *Physical Review*, **7**, 257 (1898); E. H. Griffiths, *Nature*, **56**, 258 (1897), etc.

‡ Gore, *Nature*, **25**, 473 (1882); Lord Rayleigh and Mrs. Sidgwick, *Phil. Trans.*, **175**, 458 (1884); Gray, *Phil. Mag.*, (5), **22**, 389 (1886). also **25**, 179 (1888); Shaw, *Brit. Ass. Rep.* 1886, p. 318 [*Phil. Mag.*, (5), **23**, 138]; Vanni, *Wied. Ann.*, **44**, 214 (1891); Gannon, *Proc. Roy. Soc.*, **55**, 66 (1894).

prominence with circumstances, vitiates the electrochemical equivalent of copper as it is ordinarily determined. Even a cursory study of these careful investigations shows that the complication arises at the point of contact of the copper cathode with the solution, and that the side reaction has the effect of lessening the amount of copper deposited by the current. With this in mind, we made a systematic investigation of the behavior of copper plates in cupric solutions, which led us to precisely the same conclusions as those attained by Foerster and Seidel in the paper already mentioned. Since these gentlemen have described their work in great detail, an abbreviated statement of our results will suffice.

1. Metallic copper slowly dissolves in an acid solution of cupric sulphate, even when the solution has been freed from air and has been protected by an atmosphere of hydrogen. This conclusion was tested many times, and the losses of weight of the plates were found to be roughly proportional to the respective areas of the plates, if the volume of solution was large.

2. A strongly acid solution does not differ materially in its action from a weakly acid solution; hence neither hydrogen nor  $\text{SO}_4$  ions can be responsible for the phenomenon.

3. Other things being equal, the action is proportional to the concentration of the cupric sulphate, being very slight when this is absent, even if much sulphuric acid is present. Hence the cupric ions must be the active agents, and they can only dissolve the copper according to the reaction  $\text{Cu} + \text{Cu}^{++} [+ \text{SO}_4''] \rightleftharpoons 2 \text{Cu}^+ [+ \text{SO}_4']$ . In a word, cuprous sulphate must be formed.

4. In contact with the air this action naturally takes place more rapidly than in the absence of oxygen. Instead of losing only about 0.004 milligram per square centimeter per hour in a normal solution of cupric sulphate at  $20^\circ$ , as before, the loss was nearly doubled. Evidently the cuprous becomes cupric sulphate in the oxidizing environment, and thus opportunity for further reduction is offered.

5. On the other hand, plates of copper immersed in *neutral* solutions of cupric sulphate always *gain* in weight, becoming coated with a film of cuprous oxide. This is a wholly separate phenomenon, due to the hydrolysis of the cuprous sulphate. Of course this hydrolysis cannot happen in an acid solution; hence copper deposited electrolytically from an acid solution is free from cuprous oxide. Obviously, too, the method of Vanni, which consists in adjusting the amount of acid so that the plates neither gain nor lose, is a device for replacing dissolved copper by an equal weight of cuprous oxide, and hence is very faulty from a scientific point of view.

6. As usual, the speed of these reactions is increased by increase of temperature; and moreover, the amount of cuprous sulphate which determines equilibrium is greater in a hot solution than in a cold one.

7. The addition of such substances as cane sugar, even in large amounts, produces no important effect, for obvious reasons.

8. The addition of much sodic sulphate diminishes the action, evidently by diminishing the number of cupric ions present, according to the law of mass action. In one case the loss was diminished to half its normal amount.

Many of these conclusions are to be found, either implicitly or explicitly, in the older accounts, but the interpretation of the facts is now more illuminating because of the assistance of the dissociation hypothesis. The only authority who denies the solubility of copper in cupric sulphate is Schuster,\* whose experiments involved only a very small amount of solution, which evidently required only unimportant amounts of copper for its saturation.

Foerster and Seidel have shown that it is possible to dissolve copper in a hot solution, and crystallize the metal by cooling. With the same idea in mind, we constructed an apparatus somewhat different from theirs, arranged so that this operation may take place continuously, with the production of very pure copper in beautiful minute crystals. A ring-shaped tube was fixed in a vertical plane, one side of the ring being surrounded by a steam-jacket, and the other by cool water. This arrangement naturally kept the liquid filling the tube in constant circula-

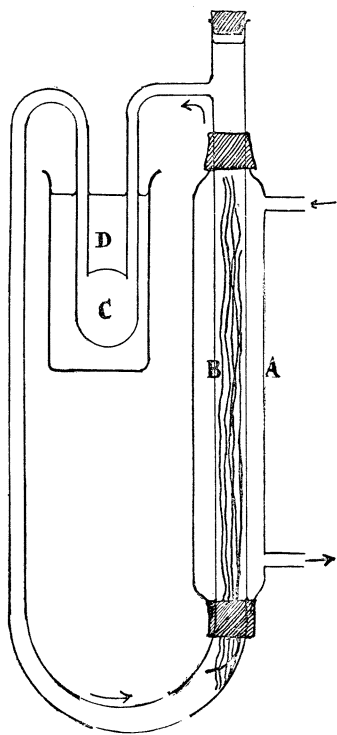


FIGURE 1. — APPARATUS FOR RECRYSTALLIZING METALLIC COPPER.

A, steam-jacket for heating copper. B, copper wires to be dissolved. C, receptacle for crystallized copper. D, cold bath.

\* Proc. Roy. Soc., 55, 84 (1894).

tion; and if an acid solution of cupric sulphate is thus made to circulate over copper placed in the hot side, considerable amounts of copper may be dissolved with ease. The crystals deposited upon cooling in the cold limb cling loosely to the glass. A more advantageous form of this device is shown in the foregoing illustration.

From these facts concerning the action of copper on a solution of cupric sulphate, the precautions necessary for obtaining the weight of deposit which most nearly represents the true electrochemical equivalent are evidently the following: —

1. The solution must be as cold as possible.
2. The solution must be acidified, to avoid hydrolysis.
3. The solution must be as dilute as is compatible with the transportation of the required strength of current to a given electrode without risk of deionizing hydrogen. The smaller the electrode, the stronger is the necessary solution.
4. Air must be excluded.

Since even at the freezing point of the saturated solution the action still takes place, although to a greatly diminished degree, the complete fulfilment of these conditions will still yield too small a deposit of copper. In order to overcome the difficulty, Foerster and Seidel \* have recommended the saturation of the solution with cuprous ions in the first place; but this plan oversteps its mark, and forms almost the only piece of faulty logic to be found in their paper. Obviously if cuprous ions were the only ones present, twice as much copper would be deposited with a given current as with pure cupric ions. It is well known that when a mixture of metals is present, that substance is deposited which gives the lowest contact-potential with the solution, provided the current is weak and the solution strong. It is easy, however, to deposit brass from a suitable solution of zinc and copper sulphates with a strong current. The present case presents some analogies to this example; but to it is added the proviso that the ions are convertible into one another, and that the cupric and cuprous salts must be present in a ratio definite for each concentration. If some of the cupric salt is removed, for example, less cuprous salt is capable of existing in the solution, and extra copper must necessarily be deposited in order to establish the equilibrium, according to the equation  $2 \text{Cu}^+ \rightleftharpoons \text{Cu}^{++} + \text{Cu}$ . Experimental verification of this reasoning will be given later.

We are then between Scylla and Charybdis, — from a cupric solution

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\* Zeitschrift für anorg. Chem., **14**, 137 (1897).

the deposit must be too small, while from a cuprous solution the deposit must be too large. Both errors decrease as the temperature decreases; but it is evidently impossible to obtain results directly with the copper voltameter which will exactly correspond with the atomic weight of copper, except by a chance combination of circumstances. This combination would be attained when the amount dissolved from the cathode by the side reaction  $\text{Cu}^{++} + \text{Cu} \rightleftharpoons 2\text{Cu}^+$  just equalled the extra amount of copper deposited from the trace of cuprous salt in the solution. Such a fortuitous condition could not be maintained for any length of time, because the amount of cuprous salt present must steadily increase by the action at the cathode as well as at the anode. At first sight, it might be supposed possible to increase the current density to such an extent that all the copper in the neighborhood of the cathode should be completely deionized; but it will be shown that hydrogen begins to be deposited instead of copper before this point can be reached.

Besides these sources of error another may exist, to which Foerster and Seidel have called especial attention. This fourth error consists in the possible semi-deionizing (or partial reduction) of the cupric salt by the electric current without the deposition of metal. Thus positive electricity may make its exit from the solution without a corresponding increase in the deposit, and the observed atomic weight of copper will be too low. Evidently, however, this action cannot result in the formation of more cuprous salt than the small proportion corresponding to its equilibrium with the cupric remaining in the neighborhood. Hence this fourth cause of error is essentially identical with the first, the simple dissolving of copper in cupric sulphate. The question then arises as to whether or not the equilibrium is established more quickly under the influence of the current than without the assistance of outside electromotive force. Both Gore and Gray, in the papers already cited, give evidence showing that reasonably small current-densities tend to increase the apparent corrosion of the copper rather than to diminish it. This might have been predicted, for it is easy to imagine that the equilibrium is established more quickly with the help of nascent cuprous ions than with the resting metallic surface of the copper plate. The authors just cited give no evidence to prove, however, that a strong current causes a less proportionate gain in weight than a weak one; indeed, Gray contends that a strong current may even *protect* the electrode from corrosion.\* The phenomena which led him to this conclusion will be shown later to be due at least in part to another cause.

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\* Phil. Mag., (5), 25, 182 (1888).

The only possible method of determining the amounts of these various modifying effects seems to be to vary the size of the exposed surface of cathode; for upon the extent of this exposed surface depend the most serious causes of error. This mode of experimentation was adopted by Shaw, and especially by Gray in the paper just cited. Gray's results are so interesting that it seems worth while to repeat a part of the plate which depicts his observations. The abscissæ register the number of square centimeters area per ampere, while the ordinates give the values proportional to the amount of copper deposited by a given current in a given time. The solution of cupric sulphate had a specific gravity varying from 1.15 to 1.18, or contained perhaps 250 grams of crystallized salt to the litre.

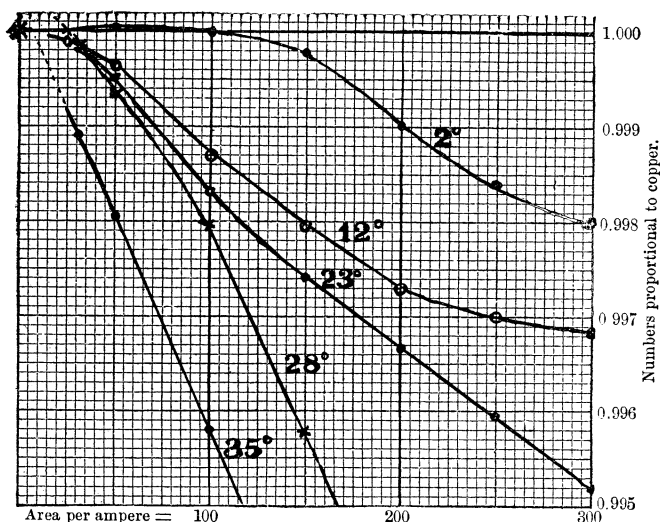


FIGURE 2.—DIAGRAM DRAWN FROM THE NUMERICAL TABLE GIVEN BY GRAY.  
(Phil. Mag., [5], 25, 182 [1888].)

It is evident that with large areas of cathode (small current densities) the fairly straight lines tend to converge at a point somewhat above the top of the table. On the other hand, when the current density becomes great, the curves fail of their mark and bend sharply to the left. Gray dismisses this remarkable tendency with the assumption of the "protective action" of strong currents already mentioned, and takes as the true value the results obtained at 2° Centigrade with current densities higher than 0.01 ampere per square centimeter.

Since it is precisely this variation of the highest values for copper which interests us, — for we know that the lower values are certainly too low, — it seemed desirable to obtain further light upon this question. We therefore carried out a similar series to Gray's, using weaker solutions, with which the point of inflection in the curve would naturally come at a lower current density. Cathodes and anodes of copper of different sizes were placed in separate portions of a solution of cupric sulphate containing 100 grams to the litre, and the same current was run through the series of cells. The amounts of copper thus deposited are given in the following table.

No. of Analysis.	Strength of Current.	Area of Cathode 50 sq. cm.	Area of Cathode 25 sq. cm.	Area of Cathode 12½ sq. cm.
	Ampere.	Grams.	Grams.	Grams.
<i>a</i>	0.12	0.07325	0.07341	0.07345
<i>b</i>	0.19	0.66856	0.66909	0.66921
<i>c</i>	0.21	0.44460	0.44469	0.44462
<i>d</i>	0.22	0.31212	0.31225	0.31204
<i>e</i>	0.25	0.45869	0.45918	0.45907

The first fact which is at once apparent is the interesting phenomenon of a *decrease* in the deposit on the smallest plate in experiments *c*, *d*, and *e*. This corresponds to a downward turn in Gray's curve; and if these results are plotted upon his scale, the following diagram is obtained. (See Figure 3, on the next page.)

Such a curve as this is only to be produced by the appearance with high current densities of another cause, independent of the cuprous-cupric reaction, but also tending to lower the observed weight of copper. It is not difficult to suggest what this cause may be. When the current increases in strength, the copper ions in the neighborhood of the cathode are no longer able to carry all of the current, and a portion of the load is taken by the only other positive ion present. But the hydrogen which thus plays the electrical rôle of the copper weighs far less than the equivalent weight of the red metal. A small amount of hydrogen, capable of being occluded by the copper without change in the appearance of the surface, would cause an immense deficiency in the gain in weight. When the current strength increases only a little above 0.02 ampere per square centimeter the deposit of the copper becomes powdery, probably because



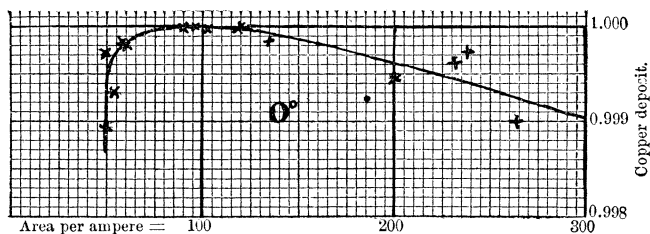


FIGURE 3. — DIAGRAM SHOWING DECREASE IN COPPER WITH SMALL CATHODES (DUE TO HYDROGEN).

The table above is here plotted by taking the highest weight of copper in each determination as unity. Great exactness could not be expected from this method, but it is sufficiently definite to show a marked deflection of the line when the 100 sq. cm. line is approached, and a sudden downward tendency when the current density approaches 0.02 ampere per square centimeter.

of the action of the occluded hydrogen, and the deficiency assumes gigantic proportions. Indeed it has been well known for a long time that this current density is the limit if one makes any pretence to accuracy; our results merely show that the action of the hydrogen begins to affect the deposit long before it becomes manifest to crude observation. Thus it seems probable that the left-handed tendency of Gray's curves, instead of being due to the approach to the true value and a lessening of the corrosion, was really due to the beginning of a new source of inaccuracy. From a theoretical standpoint such a phenomenon appears only natural; with more dilute solutions the deficiency would of course appear at lower current densities. Probably the fact that in analytical work the amount of the deposited metal never corresponds to the quantity of electricity may often be due to the same cause, in addition to the oxidizing action pointed out by Danneel.\*

Returning now to weaker currents in fairly strong solutions (Experiments *a* and *b*), it is evident both from Gray's results and from our own that the weight of the deposit in this case is approximately a linear function of the area of the cathode; in other words, the dissolving of copper in cupric sulphate is approximately proportional to the surface of copper exposed, even while the current is running. Since this is the case, the obvious method of obtaining the true weight of copper would be to extrapolate for a surface of zero area, — or to add to the weight deposited upon a medium-sized area the difference between its gain and

\* Zeitschr. Electrochem., 4, 153 (1898).

the gain on an area of twice the size. This method of correction would certainly give a correction which is too large, for during the electrolysis the solution is steadily approaching saturation with cuprous ions, which are deposited but not accounted for by the correction. Nevertheless it was decided to carry out a series of observations with plates of two sizes, calculating the results according to this method of correction, and comparing both corrected and uncorrected values with the results of an included silver voltameter. In this way an upper and a lower limit for the electrochemical equivalent of copper might be fixed; and by using a low temperature, it seemed probable that the two limits might be brought near together. Agitation would of course increase the amount of corrosion\* and diminish the error due to hydrogen; but we preferred to use low current densities and rely upon the natural convection of the electrolyte, which is then sufficient if the error is kept low by cold.

### *Experimental Details.*

The cupric sulphate used for the following experiments, after having been purified in usual ways, was allowed to stand for some time, first with flocculent cupric hydroxide and then with pure copper, in order to free it from possible traces of bismuth, silver, etc. Subsequently it was recrystallized from the purest water. Metallic copper for the anodes was prepared by electrolysis from this material, after strongly acidifying its solution with pure sulphuric and nitric acids.

The silver used for the anodes was prepared according to the well known chloride-milk-sugar method of Stas, and was amply pure enough for its purpose. The argentic nitrate used as an electrolyte was made from this silver by the action of pure nitric acid. This salt was recrystallized, dried, and fused in order to insure its neutrality. For particulars concerning these and other precautions, the reader is referred to recent papers upon the atomic weight of copper and other atomic weights.†

In any given experiment, the galvanic current was sent through two silver and at least two copper cells, all being arranged in series in such a way as to avoid liability to leakage. Every point of contact with the desk was amply insulated by glass plates, and the wires were arranged as much as possible in air-lines.

The copper cells were contained in wide-mouthed bottles with a capacity of 500 cubic centimeters each, provided with well cleaned rubber

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\* Compare Foerster's results.

† These Proceedings, **22**, 342 (1887), **23**, 177 (1887), **25**, 95 (1890), **26**, 240 (1891), etc.

stoppers. Through these stoppers ran the tubes for supplying the hydrogen used to exclude oxygen from the process, as well as the sup-

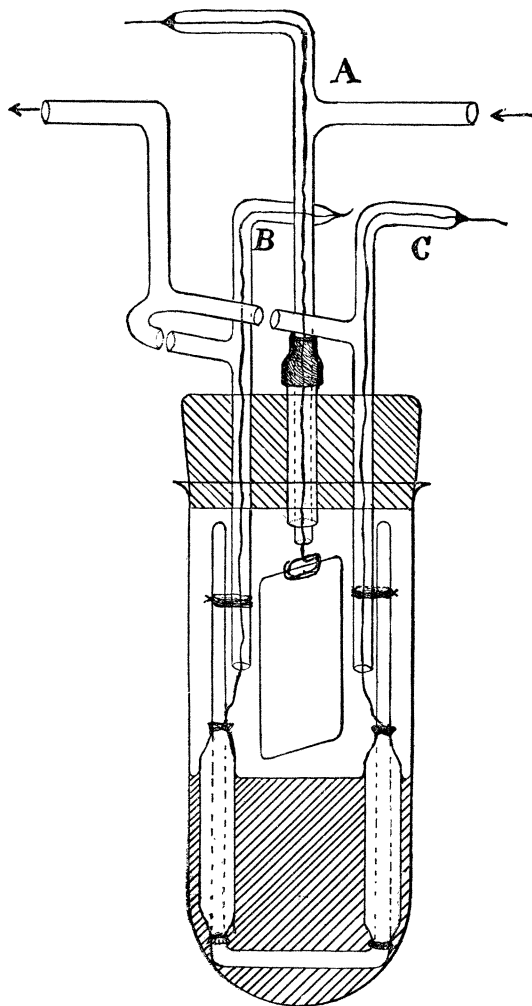


FIGURE 4.

ports for the electrodes. Two anodes (B and C) were used in each cell, and in all except the earliest experiments the cathodes (A) were of platinum. A diagram, Figure 4, while illustrating a later modification,

sufficiently explains the arrangement. At the close of an experiment the cathodes were immediately immersed in water, and after a thorough washing in pure water and alcohol were dried as usual. The electrolyte contained 100 grams of crystallized cupric sulphate in a litre.

The silver cells were essentially similar to those used by Lord Rayleigh, except that the cathodes consisted of large light platinum crucibles instead of bowls. These crucibles weighed only 60 grams, although they were capable of holding 120 cubic centimeters; they were provided with lips. A crucible exposes a smaller surface to the impurities of the atmosphere and gave in our experiments a more evenly distributed deposit than a bowl. The anode consisted of a lump of pure silver, wrapped in pure filter paper, and the electrolyte contained ten per cent of argentic nitrate. When the current was stopped the argentic nitrate was decanted through a weighed Gooch crucible, and, after standing many hours with several fillings of pure water, the crucibles

were washed with pure water and alcohol, and dried at 130°. The decantates were filtered, in order to be sure that no silver had been lost; if the Gooch crucible was found to contain any of the deposit, its weight was added to that of the greater part clinging to the cathode. In one or two of the earlier determinations, plates were used instead of crucibles as cathodes; but since the results thus obtained showed no systematic variation from those with the crucibles, the table is not complicated by calling attention to this inessential fact. The danger of losing silver mechanically from the corners of a plate is so great that this form of cathode was soon abandoned.

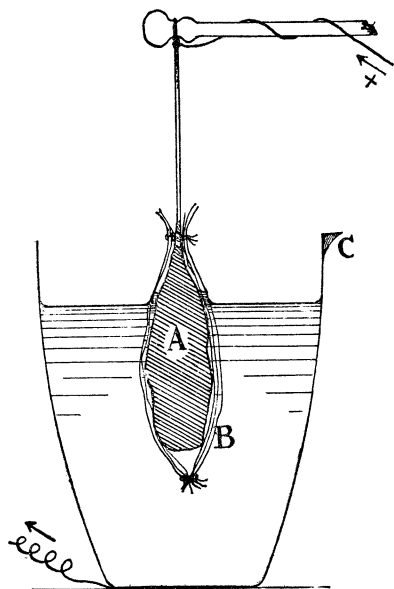


FIGURE 5. — COMMON SILVER VOLTA-METER ( $\frac{2}{3}$  natural size; section).

A, silver anode. B, filter paper covering.  
C, lip of platinum vessel forming cathode.

In the table on page 135, each horizontal line reports a complete experiment, which usually required a day for preparation and another for accomplishment. At first the copper cells were multiplied; but later when the silver seemed to be quite as uncertain as the copper, the nobler metal received its full share of representation. Some of the earlier experiments failed for one reason or another, and these failures are not included in the table. The last six determinations were consecutive; and in these the conditions of experiment were much more satisfactory than in the earlier ones; for much practice was naturally acquired in the course of the work. In all the experiments excepting Nos. 1 and 2 the cupric electrolyte was boiled and cooled to zero in an inert atmosphere before the electrolysis; and in all excepting Nos. 1, 2, 3, and 6 the copper electrolysis was conducted in an atmosphere of hydrogen.

Attention is again called to the fact that each corrected value for the copper deposit is computed from two deposits, one on a large and one on a small electrode. The exposed area of the large electrode was always about 50 square centimeters; and in all cases, except those indicated by the signs †‡ below, the area of the smaller plate was half that of the larger. The current densities varied slightly, but were always less than 0.01 ampere per square centimeter on the smaller plate, the total current strength usually being about 0.12 ampere for the system. When the total current strength was kept below this limit, no systematic variation due to its changes could be detected in the results; hence the individual figures are omitted in this published account. In order to prevent saturation with cuprous salt, the volume of the electrolyte used in each cell was fairly large, being usually about 200 cubic centimeters.

The corrected average value from the table for the atomic weight of copper, 63.563, has a "probable error" of 0.004 as far as the accidental inaccuracies of manipulation are concerned. It has already been shown, however, that a value obtained in this way must correspond to a deposit of copper slightly too great; for the mode of correction does not take account of the growing, although slight, presence of cuprous salts. On the other hand, the values computed from the directly observed quantities of copper must be too small. The average observed values, calculated from the sums at the bottoms of the respective columns, are  $\text{Cu} = 63.525$  from the larger plates, and  $\text{Cu} = 63.547$  from the smaller plates. It is evident then, that the true electrochemical atomic weight of copper, when compared with the silver deposited in the ordinary silver voltameter, must lie between the limits 63.563 and 63.547. It

## COMPARISON OF THE SILVER WITH THE COPPER VOLTAMETER.

Temperature of Silver Voltameter = 15° to 25°. Temperature of Copper Voltameter = -2° to 0°.

	Large Copper 50 sq. cm.	Small Copper usually 25 sq. cm.	First Silver (in air).	Second Silver (in air).	Corrected Copper.	Average Silver. (cor. to vac.)	Atomic Weight of Copper, Ag = 107.93.
1	0.44460	0.44469	1.51039	1.51098	0.44478	1.51064	63.56
2	0.31555*	0.31623*†	1.07476		0.31645	1.07473	63.56
3	0.24965*	0.24967*†	0.84780	0.84808	0.24968	0.84792	63.56
4	1.02182*	1.02189	3.47066		1.02186	3.47056	63.56
5	0.66090*	0.66128*	2.24545		0.66166	2.24538	63.61
6	0.62992*	0.63018†	2.14008	2.14105	0.63027	2.14050	63.56
7	0.45869	0.45907†	1.56000		0.45919	1.55995	63.54
8	0.39140	0.39165†	1.33075		0.39177	1.33071	63.55
9	1.11054	1.11042	3.76996	3.77003	1.11030	3.76990	63.57
10	0.67592	0.67578	2.29667	2.29655	0.67564	2.29655	63.51
11	0.48238	0.48235	1.63731	1.63816	0.48232	1.63768	63.58
12	0.83036	0.83064	2.82200	2.82222	0.83092	2.82203	63.56
13	0.63407	0.63449	2.15780	2.15701	0.63491	2.15735	63.53
14	0.69956	0.70029	2.37916	2.37840	0.70102	2.37868	63.61
15	0.84341	0.84375	2.86580	2.86654	0.84409	2.86608	63.57
16	0.87448	0.87455	2.97121	2.97126	0.87462	2.97114	63.54
17	0.69379	0.69392	2.35652	2.35729	0.69405	2.35683	63.57
	11.01704	11.02085			11.02363	37.43593	63.563

\* These determinations were made in duplicate. Thus, in Experiments 2, 3, and 5, four copper cells were in the current at once. The pairs agreed within themselves remarkably well, the average deviation from the mean being only 0.03 milligram.

† In these experiments, the smaller copper was  $\frac{1}{2}$  as large as the larger one.

‡ In this determination the smaller copper was  $\frac{1}{3}$  as large as the larger one.

is to be noticed that the value (63.54) obtained from Gray's observations by our method of correction is near these figures.\*

If the absolute accuracy of Faraday's law is assumed, these results show either that the silver voltameter must yield nearly 0.1 per cent too much silver, or else that the value of the atomic weight of copper found chemically in this Laboratory (63.604) must be 0.1 per cent too high.

Convincing as these conclusions seemed, the attempt was made to obtain yet further light upon the copper voltameter by varying the conditions. For example, several experiments were made with a mercury cathode, in the hope that the amalgam of copper might be less easily influenced by side reactions than the metal itself; but the difficulties in the way of determining accurately the weight of the large volume of metal which was needed to contain the copper, soon led to the abandonment of this attempt. Moreover other chemical difficulties, due to the possible dissolving of mercury, added complications.

It seemed now worth while to make a few determinations of the amount of copper deposited from a solution *saturated* with cuprous salt, in order to fix the highest possible limit for the electrochemical equivalent in a fashion wholly free from any correction, as well as to test experimentally our criticism of Foerster and Seidel's remarks about such a solution. In order to saturate the liquid with cuprous ions, the weighed platinum cathode was raised above the solution by means of its sliding support, and the current was run backward and forward for an hour or more between the two coils of copper (wrapped in filter paper, B and C, Fig. 4) which were to serve as anodes. Instead of the large bottle of the earlier experiments, a test tube just large enough to contain the electrodes was used, so that the small amount of necessary solution could be more easily saturated. In due time the cathode was lowered, and the quantitative electrolysis commenced. Of course the solution had been boiled, and was protected by a current of hydrogen throughout the experiment. The silver voltameter used was an improved arrangement, but its results are reduced to the standard used in the earlier experiments for the sake of ready comparison. This matter will be fully explained in the sequel.

This value of the atomic weight, 63.573, is 0.06 per cent higher

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\* Gray in his first paper reports that with plates of 240 sq. cm. area he obtained 0.29303 gram of copper for every gram of silver, while with plates of 50 sq. cm. area he obtained 0.29407 gram. Hence with plates of zero area he would have obtained 0.29434, corresponding to the atomic weight given above. (Phil. Mag., [5], 22, 407 [1886]. Last three determinations in table.)

COMPARISON OF THE ORDINARY SILVER VOLTAMETER WITH THE COPPER  
 VOLTAMETER SATURATED WITH CUPROUS SALT AT 0°.

	Weight of Copper (in Vacuum).	Weight of Silver (in Vacuum).	Atomic Weight of Copper.
24	0.71847	2.43935	63.578
25	0.71861	2.43940	63.585
26	0.72019	2.44603	63.556
27 <i>a</i>	0.97193	3.30100	63.558
28	0.50916	1.72859	63.582
29 <i>a</i>	0.76188	2.58664	63.580
Average . . . . .			63.573

than the average of the forty observed results in cupric solutions, and 0.016 per cent higher than these results after correction. As far as the copper deposit is concerned, this result is certainly the upper limit of the electrochemical value, although it is still below the chemical atomic weight. No experimental proof has yet been given that too much copper was deposited, however.

If the cuprous salt really carries a part of the current, it is obvious that higher temperatures, involving the presence of more cuprous salt, should raise the observed value still higher. This matter is tested in the results which follow.

 COMPARISON OF SILVER VOLTAMETER WITH COPPER VOLTAMETER SATURATED  
 WITH CUPROUS SALT AT HIGHER TEMPERATURES.

No. of Experiment.	Temperature.	Weight of Copper (Vacuum).	Weight of Silver (Vacuum).	Atomic Weight of Copper.
27 <i>b</i>	61°	0.97295	3.30100	63.62
29 <i>b</i>	55°	0.76214	2.58664	63.61

This gain in the apparent atomic weight, from 63.573 to 63.615, is conclusive. Even without further knowledge of the silver voltameter one is able to predict with reasonable certainty that higher temperatures



should yield yet higher values, and hence that the presence of cuprous salt really causes the deposit to be too heavy.

The results of all these varied operations assign a wide range of apparent values to the atomic weight of copper. In order to present the matter in a nutshell, a table is given below.

Uncorrected results of Rayleigh, Gray, Shaw, Vanni, etc.								$\left\{ \begin{array}{l} 63.30 \\ \text{to} \\ 50 \end{array} \right.$
Large plates in cupric solutions, 20° (present research,)								
"	"	"	"	0°	"	"	"	63.47
Small	"	"	"	"	"	"	"	63.525
Medium plates, in cuprous solutions,	0°	"	"	"	"	"	"	63.547
"	"	"	"	60°	"	"	"	63.573
"	"	"	"					63.615
Corrected results from cupric solutions, . . . . .								63.563
Atomic weight of copper by chemical processes, . . . . .								63.604
Discrepancy . . . . .								0.041

It has already been stated that the corrected value is probably a little too high, although it is still nearly 0.07 of one per cent below the chemical value. This discrepancy, taken in connection with the inexplicable variations in the results of parallel determinations with the silver voltameter (see page 135), led us to suspect this instrument long before the results given above were completed. Accordingly, many of the electrolyses which we have been discussing were also used as a means of testing the accuracy of the silver voltameter. The overlapping investigations have been separated in the description only in order to make a very complex matter less obscure to the reader. The outcome of the experiments upon the silver voltameter is explained below.

## II. THE SILVER VOLTAMETER.

The inference to be drawn from the preceding work is that the amount of silver deposited in the silver voltameter, as described by Lord Rayleigh and Mrs. Sidgwick\* in their classical paper, may be too great by nearly 0.1 per cent. In spite of the great care taken by these investigators, such a deviation from the exact value is not impossible; and indeed Lord Rayleigh does not claim for this work an accuracy over 0.1 per cent.

The first possible cause of error to be investigated was the possible occlusion (or rather *inclusion*) of electrolyte by the crystalline deposit.

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\* Phil. Trans., 2, 411 (1884).

Lord Rayleigh did not neglect this source of error, and by some very ingenious qualitative experiments showed that it could not be large. It seemed to us worth while, however, to analyze quantitatively the precipitated silver, and the following table recounts this series of trials, in which the silver was dissolved, and precipitated by the purest hydrobromic acid with great care.\*

No.	Silver taken (Vacuum).	Argentio Bromide obtained (Vacuum).	Silver calculated from AgBr.	Deficiency in Silver.	Percentage Deficiency.
30	0.71585	1.24567	0.71573	+0.00012	+0.017
31	5.43807	9.46557	5.43747	+0.00060	+0.011
32	3.76993	6.56216	3.76961	+0.00032	+0.008
33	2.29649	3.99820	2.29674	-0.00025	-0.011
34	2.15701	3.75473	2.15689	+0.00012	+0.006
35	2.37893	4.14187	2.37928	+0.00035	+0.015
36	2.97120	5.17218	2.97114	+0.00008	+0.003
					+0.007

The result of this table somewhat surprised us; for few crystalline precipitates contain so little included mother liquor as 0.01 per cent. While the analytical work is not perfect, (for the result of Experiment 33 can only be ascribed to accident,) one is forced to conclude that the precipitate is very nearly pure silver. Evidently the electrical method of precipitation insures a more compact structure than is possible when the precipitation does not involve outside electromotive force. One of us found three times as much water in crystallized silver prepared at 0° in another way.† The source of error in the voltameter is apparently more subtle than such a merely mechanical cause as inclusion.

Further experimentation upon such silver deposits showed that, after having been properly washed, they neither gained nor lost in weight upon continued digestion with water or with neutral solutions of ar-

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\* For the method, consult recent papers on atomic weights from this Laboratory.

† These Proceedings, **23**, 177 (1887).

gentic nitrate, hence any possible error must have crept in during the electrolysis.

The existence of flaws in the working of the silver voltameter is no new idea, and a brief résumé of earlier anomalies is necessary in order to indicate our own train of thought.

Lord Rayleigh and Mrs. Sidgwick found that large cathodes yielded higher results than small ones, and warm solutions yielded higher results than cold ones. In some cases the deviations amounted to 0.1 per cent.

Schuster and Crossley\* state that deposits made in a vacuum are slightly heavier than those produced by the same current in air, and these in turn are heavier than those produced in an atmosphere of oxygen. Myers† verified these statements. Schuster and Crossley showed also that with great current density argentic peroxide may form at the anode, and in some unexplained fashion the result is a diminution of the weight of the silver deposited; moreover, they pointed out the fact that the discrepancies observed by Lord Rayleigh and Mrs. Sidgwick between large and small bowls disappear when the anodes are of the same size. Apparently "*the anode gives rise to secondary reactions.*"

Rodger and Watson‡ observed that on continued use of the electrolyte the deposits grow heavier; and they also found that, when a very strong slightly acidified solution of argentic nitrate was electrolyzed by a powerful current, the acid was removed, and the deposit was much too heavy. They venture to say that a subsalt of silver is formed "having a silver ion heavier than the argentic salt."

Again, Kahle§ has found that after boiling the electrolyte with oxide of silver, the deposit is increased 5 parts in 10,000. In a later and very important paper|| he calls attention for the first time to the fact that in a dilute electrolyte an acid is formed during the electrolysis. Furthermore, he shows again that old solutions give too high results, an error which was sometimes removed by treatment with argentic oxide. Colored spots sometimes appeared upon the silver in old acid solutions, apparently caused by the liquid descending from the anode; these did not form in a neutralized solution, or in one which had been allowed to remain in contact with silver. Kahle's hypothetical explanation of these phenomena essentially agrees with Rodger and Watson's.

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\* Proc. Roy. Soc., **50**, 344 (1892).

† Wied. Ann., **55**, 288 (1895).

‡ Phil. Trans., **186 A**, 631 (1895).

§ Brit. Ass. Adv. Sc. Edinb. (1892), p. 148.

|| Wied. Ann., **67**, 1 (1899), or Zeitsch. f. Instrkunde, **18**, 229, 267 (1898).

The latest work which has come to our notice is that of Patterson and Guthe.\* In this paper the authors give the lion's share of their attention to an admirably worked out treatment of the physical methods necessary for fixing the electrical units, and pay little heed to the chemical side of the question. Since they obtained constant results by treating their electrolyte with argentic oxide, they recommend this method for general use, in spite of the fact that both Rodger and Watson and Kahle have shown that such treatment probably yields too high results.

The essence of all these investigations, as far as they concern the irregularities of the silver voltameter, may be summed up in the following words.

A substance which causes the deposition of too much silver seems to be formed around a large anode. Oxygen tends to eliminate this substance, hence the substance must be a reducing agent. All the phenomena agree with this interpretation. A very small anode (which causes another irregularity, namely, the formation of argentic peroxide) may result in the appearance of a lower weight of silver; perhaps argentic peroxide may oxidize the reducing substance and thus remove it. The formation of the reducing substance is accompanied by the liberation of hydrogen ions in dilute solutions of argentic nitrate; but in stronger solutions small amounts of acid may be neutralized. In warm solutions the reducing agent is somewhat more active than in cold.

An important point is left in doubt: — Does the acid appear at the anode or the cathode? Nothing could be easier than to answer this question; and a large number of trials in which the anode was enclosed in a porous cup showed conclusively that the acid was always formed at the positive pole. The solution around the cathode remained wholly neutral to methyl orange, while the liquid within the cup gave a strongly acid reaction.

In marked contrast with the case of copper, the chief disturbing reactions seem then to exist at the point at which the positive electricity enters the solution; and the obvious remedy for the irregularity is to enclose this positive electrode in a cell which will permit conductivity but will shut out convection.

#### *Experimental Details.*

Small cylinders of Pukal's porous ware (Berlin), such as are used for osmotic pressure experiments, were found to serve admirably as the

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\* Physical Review, 7, 251 (1898).

permeable septum desired. These vessels were 50 millimeters high and 20 in diameter; their walls were not much over one millimeter in thickness. Their impurities were removed by boiling with nitric acid and thorough washing with water. They were suspended in the solution by means of a platinum wire hung upon a glass hook, which insulated the

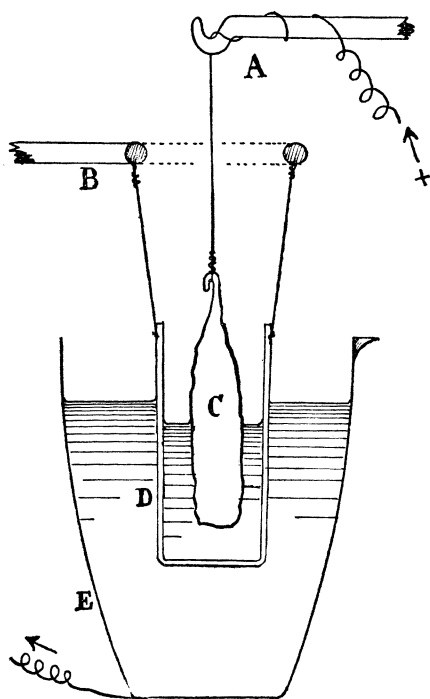


FIGURE 6. — POROUS CUP VOLTAMETER  
( $\frac{2}{3}$  actual size).

A, glass hook for supporting anode. B, glass ring for supporting porous cup. C, silver anode. D, porous cup. E, platinum cathode.

wire from the electric connections. In four experiments two concentric porous cups were used, the annular space between them being charged with argentic oxide, since Kahle found this substance to diminish the reducing action in old solutions. This last arrangement was soon abandoned, however. By means of a siphon the liquid within the cup was always kept at a lower level than that without, so as to prevent outward filtration.

The cathodes consisted of the large lipped crucibles already described; the anodes were bars  $5 \times 1 \times 1$  centimeters of the purest silver, supported by silver wires and not enclosed in filter paper; and the electrolyte usually contained 10 per cent of pure freshly prepared argentic nitrate.

The temperature of the cell under investigation was kept constant by means of

suitable baths. For a low temperature a mixture of pure ice and a solution of ammoniac nitrate answered well, and for the higher temperatures a large beaker containing pure water was warmed from the outside by enough encircling leaden steam-pipe to cause the desired intensity of heat.

The manipulation was simple. The platinum crucibles were cleaned, dried at  $160^{\circ}$ , and weighed after two or three hours' cooling in a large desiccator kept in the balance-room. In order to prevent leakage during the electrolysis, the several stands were insulated by separate glass plates, and all the connections were air lines. The apparatus was protected, as in the earlier experiments with copper, by a miniature house with walls of fine cotton cloth, which helped to exclude dust. When the current was broken, the electrolyte was removed, the silver was rinsed twice with water, a third filling with water was allowed to stand in the crucible for two or three hours, and a fourth one remained in it over night. The wash-waters were collected and filtered if the silver showed any tendency to break off. In such cases a Gooch crucible was employed to collect the particles; and a very small filter, afterwards burned, served to catch the minute flakes of asbestos detached from the mat. On the next morning, the crucibles were washed once more, rinsed twice with pure alcohol, and finally dried and weighed as before. This method of treatment gave opportunity for the diffusion of mother liquor from the intricate recesses of the crystallized mass, while it did not run the risk of dissolving silver which may attend the use of boiling water for washing. It is probable that traces of water remained even after drying at  $160^{\circ}$ , but the experiments on page 139 show that these traces were less than one part in ten thousand.

Weighings were made upon the balance which served for the weighings in the earlier work upon copper, — one which has served also for many determinations of atomic weights. Its results with small objects may be depended upon to within  $\frac{1}{10}$  milligram. All weighings were made by double substitution, a similar vessel being used as a tare, and the weights were of course carefully standardized. Since the question concerned merely the comparison of silver with silver, the results were not corrected to the vacuum standard.

The object of the work described below was to determine the relative values given by the silver voltameter under different conditions, and to interpret the results in such a way as to point out the true value. For such a purpose it is convenient to select some one method as a standard of reference; and because the porous cup method, conducted at  $20^{\circ}$ , soon showed itself to be capable of giving the most constant results of all the various modes of procedure, it was chosen as this standard. For example, in one case a given current caused depositions of 2.43744 and 2.43749 grams of silver in two cells placed in series, — a difference of only 2 parts in 100,000.

## THE SILVER VOLTAMETER UNDER VARYING CONDITIONS.

Number of Experiment.	Weight of Silver (standard). Cell at 20°-25°.	Weight of Silver in Voltameter to be tested.	Difference.	Ratio of standard Silver to heavier Silver.	Method used in Voltameter to be tested.
	Grams.	Grams.	Milligrams.		
37	1.94124	1.94267	1.43	1.00074	Cathode a lipped crucible; anode wrapped in filter paper; precisely like the cell used in preceding copper work.
38	1.76283	1.76425	1.42	1.00080	
39	3.04996	3.05270	2.74	1.00090	
			Average = 1.00081		
40	3.09629	3.09918	2.89	1.00094	Lord Rayleigh's method. Cathode a bowl; anode a plate in filter paper; at 20°±.
41	2.53256	2.53439	1.83	1.00072	
			Average = 1.00083		
42	2.53256	2.53357	1.01	1.00040	The same at 0°.
				[1.0012]	The same warm.*
43	2.55012	2.55460	4.48	1.00176	Patterson and Guthe's method; old electrolyte saturated with Ag <sub>2</sub> O.
44	1.89800	1.90238	4.38	1.00230	
			Average = 1.00203		
45	2.44412	2.44599	1.87	1.00077	Cathode a crucible. Anode enclosed in porous cup like standard, but temperature 60° (instead of 20°).
46	3.29842	3.30036	1.94	1.00059	
			Average = 1.00068		
47	2.63668	2.63822	1.54	1.00058	Like the above, except that two porous cups packed with Ag <sub>2</sub> O isolated the anode (60°).
48	1.72724	1.72724	0	1.00000	
49	2.58463	2.58663	2.00	1.00078	
50	3.09629	3.09988	3.59	1.00116	
			Average = 1.00063		
51	2.55012	2.55029	0.17	1.00007	Cathode a crucible. Anode enclosed in porous cup like the standard. Temperature 0°.
52	1.89800	1.89845	0.45	1.00024	
			Average = 1.00016		

\* From Lord Rayleigh's figures.

With this cell were compared the following modifications of the silver voltameter: first, the large crucible voltameter at  $20^{\circ}$ , with the anode wrapped in filter paper, such as was used in the preceding experiments upon copper; secondly, a voltameter at  $20^{\circ}$  prepared according to Lord Rayleigh's standard prescription (a platinum bowl, 10 centimeters in diameter, containing a 15 per cent solution of argentic nitrate and a large silver plate enclosed in filter paper); thirdly, the same arrangement at  $0^{\circ}$ ; fourthly, an exact imitation of Patterson and Guthe's method, for which the electrolytes used in Lord Rayleigh's method were digested with argentic oxide and filtered; fifthly, the "porous cup method" at  $60^{\circ}$  instead of at  $20^{\circ}$ ; sixthly, the same with a double porous cup enclosing argentic oxide in the annular space; and finally, the "porous cup method" at  $0^{\circ}$ . The table opposite explains itself.

### *Discussion of Results.*

The comparison of these results is highly instructive. The most noticeable fact is that our "standard porous cup method" gives the lowest result of any of the methods tried, since all the figures in the fifth column are greater than unity. In the next place, we find that Patterson and Guthe's method gives a result 0.12 per cent higher than Lord Rayleigh's; a figure which corresponds closely with their own estimate, 0.11 per cent, while Lord Rayleigh's method gives results 0.082 per cent higher than ours. Evidently the method used in the first three experiments is essentially similar to Lord Rayleigh's, and may be averaged with it. Again, it is apparent that the interposition of argentic oxide in the hot determinations had a varying and unsatisfactory effect, as if it introduced a new source of error. Finally, it appears that change of temperature causes a somewhat smaller variation in the results from the "porous cup method" than in those from Lord Rayleigh's old standard:—

	Lord Rayleigh's Voltameter.	Porous Cup Voltameter.
$60^{\circ}$	1.0012 (?)	1.00068
$20^{\circ}$	1.00083	1.00000
$0^{\circ}$	1.00040	1.00016

The obvious inference from these facts is that the porous cup is really effectual in protecting the cathode from a part at least of the disturbing influences under consideration, especially at low temperatures. The apparent *gain* of 0.016 per cent exhibited by the method at  $0^{\circ}$  was undoubtedly due to the difficulty in washing the very finely divided spongy metal which is deposited from a freezing solution; but Lord Rayleigh's



method at  $0^{\circ}$  is affected by the same source of error, so that the comparison is a fair one.

The only alternative to this inference, — the supposition that the porous cup introduces a new complication causing too low a weight, — is difficult to disprove; but, on the other hand, the possible nature of such a complication is not easily conceivable.

Recurring to the first inference, an hypothesis supported by many facts, we admit it to be probable that the porous cup does not wholly prevent the admixture of the hypothetical complex ions with the liquid around the cathode; for even if diffusion were wholly prevented, some of these ions might migrate with the current. Both diffusion and migration are increased in rapidity by a rise in temperature, hence even with the porous cup the hot solution gives a somewhat higher value.

It is a matter of great interest to study the effect of the low value obtained by the new method upon the electrical atomic weight of copper, upon the electrolytic value assigned to the ampere, and upon the electrical result for Joule's equivalent.

We concluded, at the close of the section devoted to copper, that the atomic weight of this metal must lie between the limits 63.547 and 63.563, if the common silver voltameter is correct in its verdicts. We have now shown that the results of this voltameter are in all probability too high by 0.081 per cent; hence the conclusion is that the true atomic weight of copper must lie between 63.598 and 63.615. Since the elaborate chemical investigation of copper carried out some years ago in this Laboratory yielded the value 63.604, we have here a remarkable confirmation of the results of the "porous cup voltameter."

In this connection, it is worth while to call attention to the reasons why copper placed in an ice-cold solution of argentic nitrate causes the deposition of the true amount of silver.\* Of this automatic voltaic cell the anode is copper; hence the complications which arise around a silver anode do not exist. On the other hand, the cathode is silver; hence the complications which take place around a copper cathode do not exist. The trace of cuprous salt undoubtedly formed at the anode does not decompose the very cold ions of nitric acid, but sooner or later deposits its equivalent of silver. The action is so slow at the low temperature that the current density where the silver is deposited is very small, hence there is no danger of the deposition of a weighable amount of copper

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\* Richards, These Proceedings, **22**, 342, **23**, 177 (1887).

with the silver; \* and the concentration effect prevents the deposition of silver in any place where the silver has become nearly exhausted from the solution.

It is possible to apply a correction to the various values which have been assigned to the electrochemical equivalents of copper and silver with the help of the tables given above.

This computation is made below; it does not pretend to be precise, but will show in a general way the effect of the complications under consideration.

	(Grams per Ampere-second.)
Lord Rayleigh and Mrs. Sidgwick . . .	$\frac{0.0011179}{1.00082} = 0.0011170 \dagger$
Fr. and W. Kohlrausch . . . . .	$\frac{0.0011183}{1.00082^{(?)}} = 0.0011174$
Kahle (fresh solutions) . . . . .	$\frac{0.0011182}{1.00082} = 0.0011173$
Patterson and Guthe . . . . .	$\frac{0.0011192}{1.00203} = 0.0011174$

The average of these results is about 0.0011173, but perhaps 0.0011172 (the mean between the two extremes) is a safer value to choose.

From this value of the electrochemical number for silver, that for copper may be calculated simply by multiplication with the ratio of the chemical equivalents; for we have shown that its true value corresponds to Faraday's law within one part in five thousand. Hence it may be taken as  $0.0011172 \times \frac{63.604}{215.86} = 0.0003292$  grams per ampere-second. ‡

\* Lord Rayleigh and Mrs. Sidgwick, *Phil. Trans.*, **175**, 470 (1884).

† The probable reason for the lowness of this result is the fact that Lord Rayleigh washed and ignited the silver at high temperatures. All the other values, including our own, may be a trifle high because of traces of occluded mother liquor. No attempt is made at present to correct the results for this possible error. The results of Masquart (*J. de Phys.*, [2], **3**, 283 [1884]), Pellat and Potier (*Ibid*, [2], **9**, 381 [1890]), Köpsel, Heydweiller, and others are omitted from this table, since they throw no further light chemically. Some are too low and others too high, hence they would not have much effect on the average. Compare Patterson and Guthe's paper.

‡ The value 0.0003294 found by F. E. Beach from a solution containing chlorine is probably affected by the presence of cuprous salts. (*Am. J. Sc.* [3], **46**, 81 [1893].) All the other directly determined values for this quantity are lower than our value.

Thus 96,610 coulombs correspond to one gram equivalent of an electrolyte.

These numbers are of interest from a theoretical standpoint, but their practical value as means of determining current strength must depend upon the ease of their application. The value for copper is a mean between two limits, and is not easy to reproduce with exactness; but for most purposes the weight deposited by current densities between 0.008 and 0.012 amperes per square centimeter, from ten per cent solutions of cupric sulphate cooled below zero and protected by an inert atmosphere, is sufficiently close to the real value. Nevertheless, empirical tables like those of Gray will probably remain the most convenient method of computing current strength from the deposition of copper.

On the other hand, the intricacy added by the porous cup in the silver determination is not serious, and the results obtained seem trustworthy. Obviously any method capable of being repeated with constant results, when standardized with accuracy by means of known currents, would serve all practical purposes; and a method which is constant because the sources of error have been at least partially removed is certainly worthy of attention.

This point suggests a discussion which has recently arisen concerning the electrical determination of Joule's equivalent, which depends upon measuring the heat corresponding to a known amount of electrical energy. Griffiths, in an appendix\* to an elaborate paper† upon this subject, calls attention to the fact that an error in the electrochemical equivalent of silver of 0.1 per cent would explain the difference between his value of the mechanical equivalent of heat and Rowland's. The equation of Griffiths for the calculation of his value is

$$J = \frac{E^2}{RM} \left( \frac{\delta t}{\delta \theta} \right),$$

in which  $E$  signifies the constant potential difference,  $R$  = the resistance converting electricity into heat,  $M$  the heat-capacity which is heated,  $\delta t$  the interval of time, and  $\delta \theta$  the change of temperature. The electrochemical equivalent of silver enters into this expression in the determination of the value of  $E$  in reference to  $R$ . Griffiths's value for  $J$  is larger than Rowland's, hence his value for  $E$  is greater than that which Rowland would have observed if he had used an electrical method; or, in other words, too small an amount of silver may have been taken as the

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\* Nature, 56, 258 (1897).

† Proc. Roy. Soc., 53, 6 (1893).

amount corresponding to the ampere in computing Griffiths's *E*. Such an inaccuracy may have come about in two ways: either the electromagnetic methods for determining the *energy* of an ampere may have caused the original investigators of the ampere equivalent to overestimate the strength of their current, or else they may have used a form of voltameter which gave a smaller deposit of silver than the form used by Glazebrook in standardizing Griffiths's cells. This last supposition is the only one with which the voltameter is concerned, for it is clear that a *constant error* in the amount of silver, occurring both in the original comparison of the ampere value, as well as in the standardizing of Griffiths's cells, could have no effect,—the weight of silver would be eliminated from the result. The only safe mode of comparing results of this kind is to reduce all figures to the standard of some one form of silver voltameter, capable of giving constant values, as has been done above. Patterson and Guthe, in their otherwise valuable paper, do not seem to realize this fact, and only add to the confusion by appearing to suppose that the results with their plethoric voltameter are directly applicable to Griffiths's equivalent. (See line 4, p. 281 of their paper in the *Physical Review*, Vol. 7.)

This paper is by no means a final statement of the matters which it concerns. It is in the nature of a preliminary contribution, and we intend now to test more rigidly the accuracy of the "porous cup voltameter," as well as to study from a physico-chemical standpoint the cause of the anomalies which are rendered harmless by its use. Some light has already been obtained, and more seems not far off.

#### SUMMARY.

In conclusion, a brief summary of the chief points treated in the paper may serve as an index to the more intricate details.

1. Metallic copper dissolves in cupric sulphate with the formation of cuprous sulphate, and unless acid is present cuprous oxide or hydroxide is formed by hydrolysis; in short, most of Foerster and Seidel's results are confirmed.

2. On the other hand, the saturation of the solution with cuprous salts is shown to cause too high results in the copper voltameter.

3. Vanni's method of correcting the copper voltameter by regulating the amount of acid present is shown to be unsound, although its results are not very erroneous.

4. Before the cupric solution is made so dilute that its solvent action

becomes negligible with a given current density, the deposition of hydrogen interferes with the exact determination of the electrochemical equivalent, even before hydrogen is actually evolved in bubbles. Hence the use of a small cathode is dangerous beyond a limit which depends upon the accuracy required. With small current density an approximate correction may be made for the area of the cathode.

5. Some possible causes of error in the silver voltameter are obviated by a simple device; and with the help of this apparatus the older methods are compared with one another. The danger of a fallacy in such a comparison is pointed out.

6. The electrochemical equivalent of silver appears to be about 0.0011172 gram per ampere per second.

7. The electrochemical equivalent of copper appears to be between 0.00032915 and 0.00032925 gram per ampere per second.

8. The discrepancy between the chemical atomic weights of copper and silver and their electrochemical equivalents is explained; hence Faraday's law is verified with two cathions more precisely than before. Conversely, assuming Faraday's law to hold rigidly, and the value 63.60 to represent the true atomic weight of copper, the agreement furnishes evidence of the accuracy of the new method.

HARVARD UNIVERSITY, CAMBRIDGE, MASS.,  
October 14, 1899.